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# CHARACTERIZATION OF DIAMOND FILMS BY THERMOGRAVIMETRIC ANALYSIS AND INFRARED SPECTROSCOPY

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## ABSTRACT

*Micron 4.1 Silicon Micrometer*  
→ Diamond films were grown on S wafers at about 3 um/hr by microwave plasma assisted chemical vapor deposition. The infrared transmission of a 3-um thick film varied from near 61% at 5000/cm<sup>-1</sup> to near 75% at 1000/cm<sup>-1</sup>. Thermogravimetric analysis indicated that the diamond films oxidize in air at about 650°C and are less resistant to oxidation than graphite. A film containing nitrogen was grown by adding N<sub>2</sub> to the feed gas.

MATERIALS INDEX: diamond

## Introduction

*Start* → Recent advances in the growth of diamond films by low pressure chemical vapor deposition (CVD) have generated a great deal of interest in developing diamond materials for a variety of technological applications. (1) Unique optical, thermal and mechanical properties make diamond the material of choice for many purposes. A technique involving microwave plasma assisted chemical vapor deposition for the growth of diamond films was described recently by Chang, et. al. (2). Here, we report results obtained in characterizing free-standing diamond films produced by this technique.

## Experimental

Depositions were conducted by introducing a gaseous mixture of 2.1% methane and 1.0% oxygen (vol/vol) in hydrogen through a 12.5-mm diameter quartz tube into a plasma sustained in a 2.45 GHz Evenson microwave cavity (2). A 1-2 cm<sup>2</sup> Si (100) wafer was placed directly in the plasma. The reactor pressure was maintained at 21 torr and microwave power was 170 W. No external control of the substrate temperature was provided. The substrate was seeded by rubbing together two pieces of silicon dusted with industrial diamond powder (<0.5- $\mu$ m diameter) and then scraping off nearly all of the diamond powder with a razor blade. Continuous films formed with a growth rate of about 1 mg/hr. Free-standing films were obtained by soaking the film/Si substrate overnight in a 55% HF aqueous solution.

### Results and Discussion

A film grown for 1 hr had a maximum thickness of 3  $\mu$ m and was translucent and slightly gray. The side exposed to the plasma during deposition had a dull appearance while the side next to the substrate during deposition had a smooth reflective appearance. A 7-hr deposition gave a very similar film that was somewhat darker with a bronze tint. The maximum thickness was 20  $\mu$ m. The films curled slightly away from the substrate upon detachment, indicating compressive stress in the films resulting from the thermal expansion mismatch between the films and the Si substrates.

The Raman spectrum (488-nm incident light, 100- $\mu$ m beam diameter) of the 3- $\mu$ m film exhibits a sharp peak at 1331 cm<sup>-1</sup> indicative of diamond (3-5), and a broad peak near 1520 cm<sup>-1</sup> for non-diamond carbon (Figure 1). Similar Raman spectra were obtained throughout both the 3- and 20- $\mu$ m films, indicating homogeneity. The morphology of the films from scanning electron micrographs is characterized by up to 2  $\mu$ m facets on the growth side while no facets are observed on the side of the film that was against the substrate during growth. The films exhibited X-ray diffraction lines at  $d = 2.057$ , 1.259, and 1.075 Å, in excellent agreement with values for natural diamond (2.060, 1.261, and 1.075 Å)

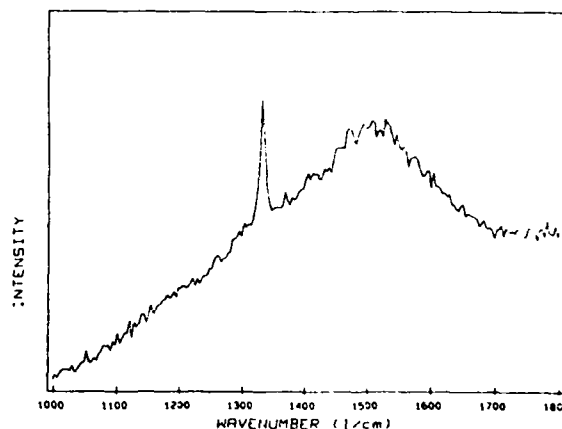


FIG. 1  
Raman spectrum of free-standing  
3- $\mu$ m diamond film.

and synthetic diamond films (6). The presence of diamond in the films was also confirmed by Auger electron spectra which exhibited fine structure in the carbon KLL line characteristic of diamond (7).

Transmission Fourier transform infrared spectra of the films are shown in Figure 2. From the spacing of interference fringes and assuming a constant refractive index of 2.38 we calculate thicknesses of 3.0 and 13  $\mu\text{m}$  for the two samples (8). The transmission of both films near 10  $\mu\text{m}$  is 75% based on the geometric mean of maximum and minimum transmittance from the interference fringes (8).

However, the maximum transmission of the 3- $\mu\text{m}$  film is 102% at 13.7  $\mu\text{m}$ . This indicates that there is an instrumental error in the transmission measurement of at least 2% and that the actual transmission of the films is probably at most 73%.

The maximum transmission expected for a film with smooth surfaces and an index of refraction of 2.38 is 71.4% (9). This discrepancy could be accounted for by instrumental error or by a lower value for the refractive index (A film with an index of refraction of 2.31 would have a maximum transmittance of 73%). Since the transmission of the 3- and 13- $\mu\text{m}$  films is about the same at 10  $\mu\text{m}$ , there is clearly very little absorption at this wavelength. The decrease in amplitude of the interference fringes at shorter wavelengths and the generally smaller amplitude for the 13- $\mu\text{m}$  film can be attributed to surface roughness and non-uniform thickness (10). The decrease in transmittance at shorter wavelengths is more pronounced in the thicker film and this probably reflects increased bulk scattering and perhaps absorption in the thicker film. Figure 3 shows an expanded view of the C-H stretching region. Absorption peaks appear at 3325  $\text{cm}^{-1}$  (assigned to C-H stretching involving carbon with  $\text{sp}$  hybridized bonding) and from 2925 to 2830  $\text{cm}^{-1}$  (assigned to C-H stretching involving  $\text{sp}^3$  bonded carbon CH or  $\text{CH}_2$  groups) (11-13). The feature at 2925-2830  $\text{cm}^{-1}$  is nearly identical to that reported by Kobashi, et al. (6). The peaks are much more intense for the 13  $\mu\text{m}$  film indicating that the C-H groups are located in the bulk of the film and not confined to the surface. The presence of  $\text{sp}$  and  $\text{sp}^3$  carbon species in the films is consistent with proposed growth mechanisms involving acetylene (14) or methyl radical (15), both of which

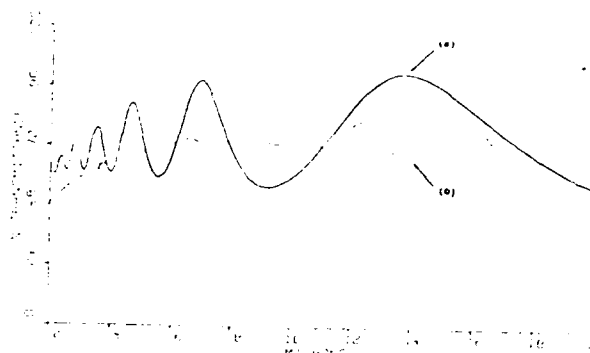


FIG. 2  
Infrared transmission spectra of free-standing diamond films: (a) 3- $\mu\text{m}$  film, (b) 13- $\mu\text{m}$  film.

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are known to be present in the gas phase (16,17). It is interesting to note that absorption from  $sp^2$  bonded carbon C-H groups was not observed in our films even though  $sp^2$  bonded carbon is generally thought to be the major contaminant in diamond films based on Raman data.

Thermogravimetric analyses were carried out on diamond films, diamond powder (<0.5- $\mu\text{m}$  diameter), and graphite powder (2-20  $\mu\text{m}$  average dimension) in air at pressures of 710 and 50 torr, and at a constant heating rate of 20°C/min, Figure 4. The diamond powder oxidizes at the lowest temperature, the films at an intermediate temperature, and graphite powder at the highest temperature.

Discrepancies in the low weight regions of the data are due to instrument drift and result from the low sample weights (~1 mg) analyzed. The rate of oxidation, indicated by the rate of weight loss, is similar for the films at both 710 and 50 torr air pressure, while the rate of oxidation of the diamond powder is increased significantly at 710 torr as compared to 50 torr. Thus, the oxidation rate of the diamond powder is limited by ambient  $O_2$  concentration, while the oxidation rate of the diamond film is limited by surface area exposure to ambient  $O_2$ . We believe that the lower oxidation temperature of the diamond powder versus the diamond film reflects the higher surface area of the powder. Figure 5 shows the weight loss of a 2.1-mg diamond film (7- $\mu\text{m}$  average thickness) when heated according to the following temperature program: 25-500°C at 40°C/min, 500-600°C at 10°C/min, hold for 120 min, 600-700°C at 10°C/min, hold for 60 min. The rate of weight loss at 600°C declined over the first 60 min and reached a nearly constant value of 1.5%/hr over the second 60 min. Initial rapid oxidation has also been observed for synthetic diamond powders (18). At 700°C the rate of weight loss reached a constant value of 1.0%/min. The corresponding weight loss rate in  $\mu\text{m/hr}$  is 0.1  $\mu\text{m/hr}$  at 600°C and 4  $\mu\text{m/hr}$  at 700°C. The oxidation rate of the (100) face of natural diamond was found to be approximately 0.2  $\mu\text{m/hr}$  at 600°C and 6  $\mu\text{m/hr}$  at 700°C (19). It is interesting that the weight loss was constant

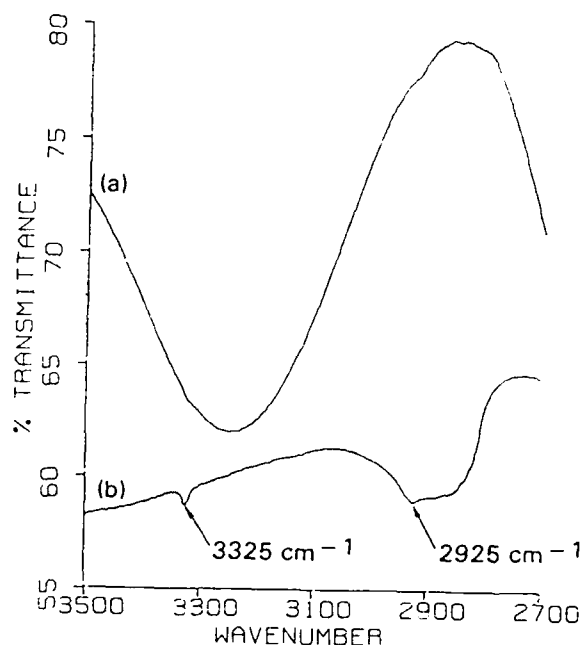


FIG. 3  
Infrared transmission spectra  
in the C-H stretching region of  
(a) 3- $\mu\text{m}$  film, (b) 13- $\mu\text{m}$  film.

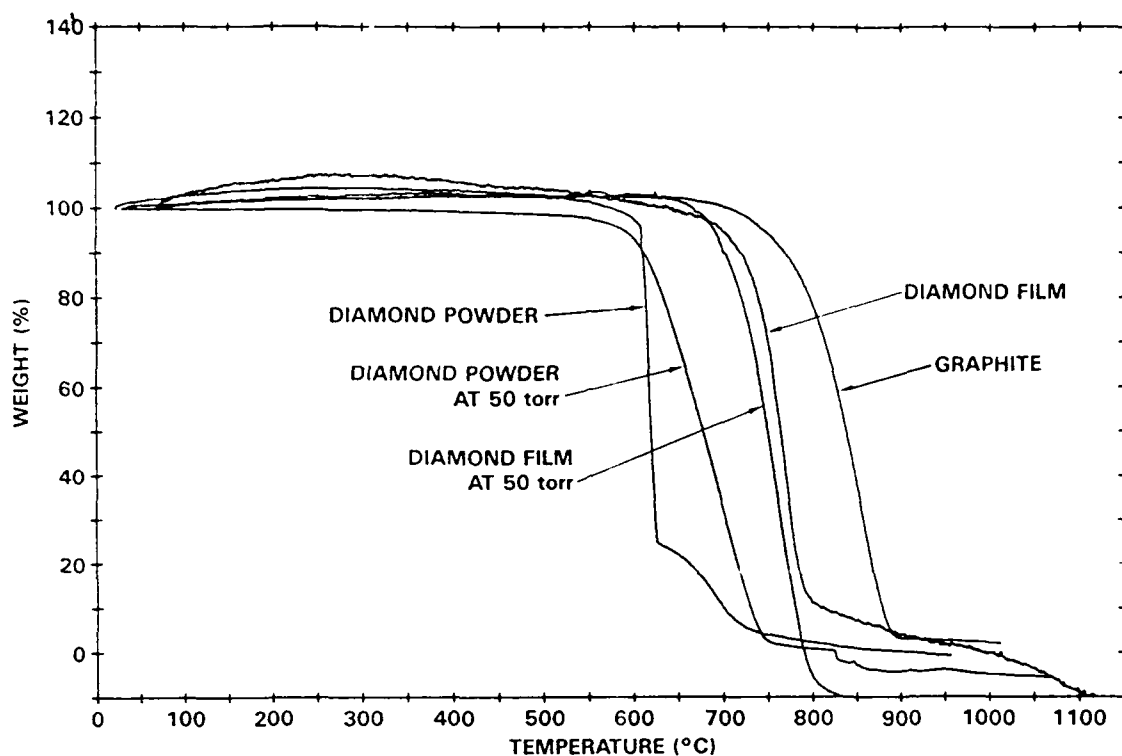


FIG. 4. Thermogravimetric analysis in air of diamond powder at 710 and 50 torr, diamond films at 710 and 50 torr, and graphite powder at 710 torr.

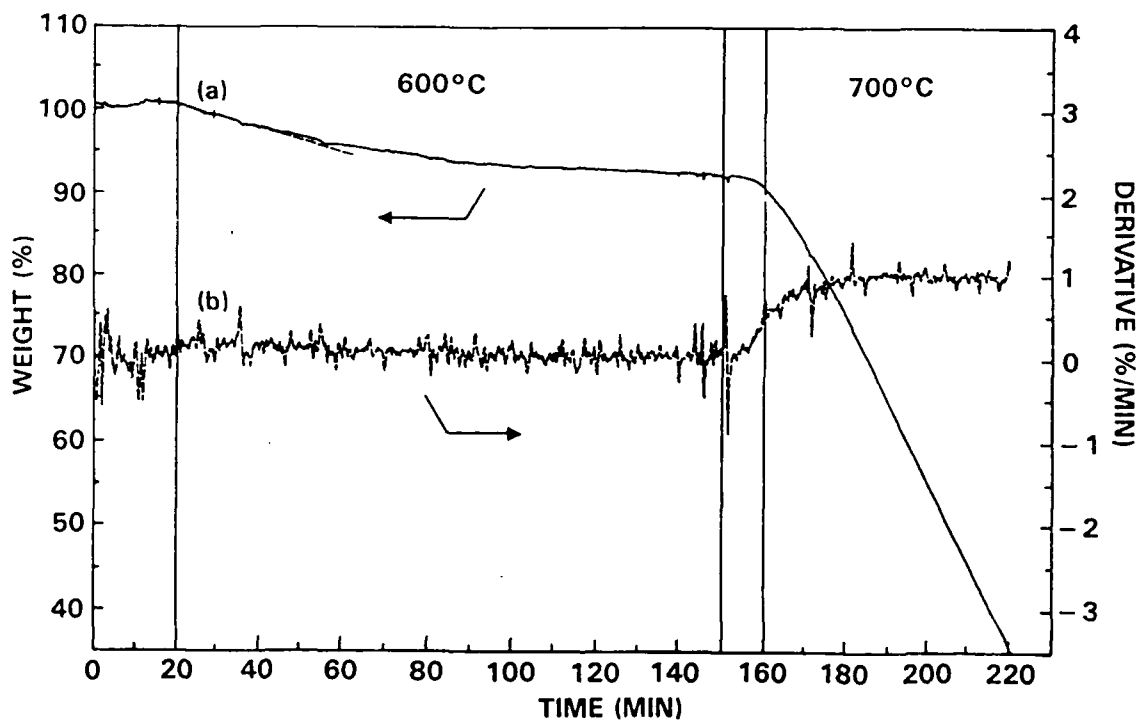


FIG. 5. Thermogravimetric analysis of a 7-μm film at 600°C and 700°C: (a) weight percent vs. time curve, (b) derivative of curve (a).

at 700°C even though the sample was reduced to 35% of its original weight. This probably reflects a nearly constant surface area of the sample due to the film becoming thinner during oxidation. Our results agree with previous studies showing that graphite oxidizes at a higher temperature than diamond (18,20), and that the oxidation rate of synthetic diamond increases for smaller particle size (21).

Electron spin resonance (ESR) reportedly gives an indication of the quality of diamond films (22). Films deposited by CVD exhibited an ESR signal at  $g=2.0027$  with linewidths varying from 6.1 to 3.0 G. Films that show the strongest diamond Raman signal at  $1333\text{ cm}^{-1}$  gave the narrowest ESR linewidth. Our film exhibited a strong featureless signal in Figure 6a at  $g=2.002$  with a peak-to-peak linewidth of 2.5 G, even sharper than the previously reported linewidths. Traces in 6b and 6c demonstrate that adding 0.3%  $\text{N}_2$  to the feed gas stream leads to incorporation of nitrogen atoms in the diamond film. Figure 6c is the spectrum of synthetic diamond powder used to seed the film growth. It is similar to the spectrum of diamond powder reported previously (22). Two overlapping 3-line spectra appear with coupling constants of  $3.82 \times 10^{-3}$  and  $2.76 \times 10^{-3}\text{ cm}^{-1}$ , in good agreement with literature values of  $3.80 \times 10^{-3}$  and  $2.71 \times 10^{-3}\text{ cm}^{-1}$  for the "P1 center." (23,24). The defect that gives this spectrum is a nitrogen atom occupying a carbon lattice site in diamond. The spectrum of diamond powder in Figure 6c is a superposition of the P1 center and an additional signal at the center of the spectrum. The spectrum of diamond film grown in the presence of nitrogen, Figure 6b, shows the P1 center plus two

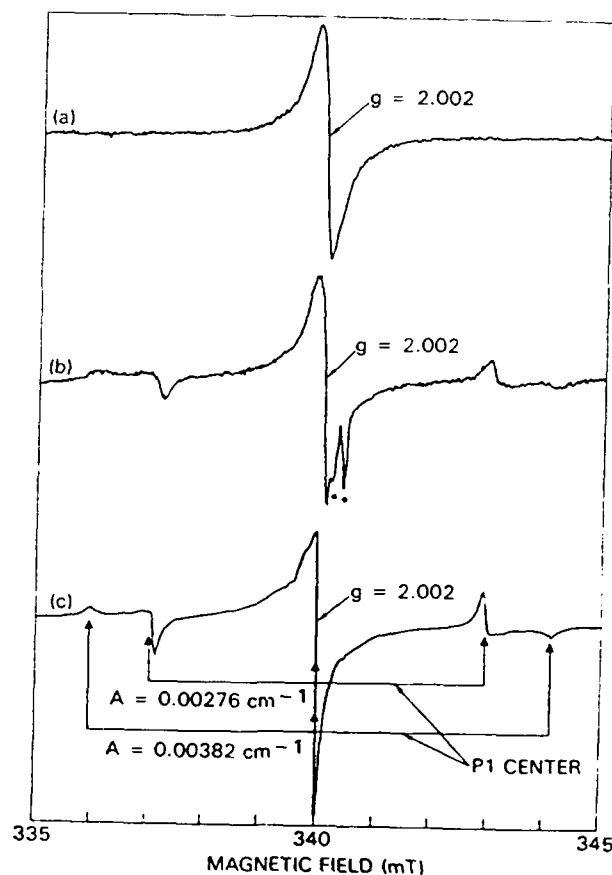


FIG. 6  
ESR spectra of: (a) 1.5-mg diamond film grown from  $\text{CH}_4$  in  $\text{O}_2/\text{H}_2$ , (b) 0.4-mg diamond film grown from  $\text{CH}_4$  in  $\text{O}_2/\text{H}_2$  plus 0.3% (vol/vol)  $\text{N}_2$ , (c) diamond powder used to seed film growth. Spectra were recorded at room temperature at 9.52 GHz with microwave power in the range 2-70 mW and modulation amplitude in the range 0.3-0.8 G.

unidentified signals indicated by asterisks that must arise from additional defects not found in the film that gave trace 6a.

### Conclusion

Free-standing diamond films were produced by microwave plasma-assisted chemical vapor deposition. The infrared transmission at long wavelengths is close to the maximum expected for diamond films. C-H group impurities are consistent with proposed diamond growth mechanisms involving carbon species containing either sp or sp<sup>3</sup> bonded carbon. The diamond films oxidize in air at about 0.1  $\mu\text{m/hr}$  at 600°C and 4  $\mu\text{m/hr}$  at 700°C. A diamond film containing nitrogen was grown by adding N<sub>2</sub> to the feed gas.

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